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Uncertainty in Measurement of Isotope Ratios by Multi-Collector Mass Spectrometry

Abstract

Multi-collector mass spectrometry, both inductively coupled plasma source (ICPMS) and thermal ionization source (TIMS), can measure isotope ratios with great precision because the ion beams from different isotopes are measured simultaneously with different detectors. Accurate isotope ratio results require that the measurement system be fully understood. Accounting for all sources of uncertainty in such analyses, according to JCGM *Evaluation of measurement data — Guide to the expression of uncertainty in measurement* (GUM), requires understanding the characteristics of the ion beam, and the instrument response. Modern multi-collector mass spectrometers record multiple electronic integrations of ion beam signals for a set time period, for example 5 seconds, and ratios of these signals on two detectors are calculated. The standard uncertainty on the mean of these ratios, a measure of the repeatability, is an important part of the combined standard uncertainty, but it is only one component. Often, the instrument software embeds constants and calculations in the data that is recorded, and post data acquisition processing introduces other variables. All of these constants and variables that are corrections to a measurement must be considered in the treatment of uncertainty. A general equation for an isotope ratio measurement by multi-collector mass spectrometry is presented which considers the most common of these corrections. Accurate calculation of the combined standard uncertainty using this equation requires that the standard uncertainties for the individual ion beam signals be defined. However, the dispersion of these signals as calculated by standard statistical methods does not necessarily reflect the excellent repeatability of the ratio measurements, which is the hallmark of multi-collector instruments. To capture this repeatability it is necessary to partition the standard uncertainty on the ratio measurement between the signals for the numerator and denominator isotopes. An equation for this partitioning, and the sensitivity coefficients for all of the variables and sub-functions of the general equation are given.

1. Introduction

IAEA safeguards requires that isotopic measurements of uranium and plutonium be made of various samples for purposes of material accountability, compliance monitoring, or detection of non-compliance with a treaty, an agreement, or a facility declaration. In order for these measurements to be not only complete, but useful for their purpose, they must include a statement of uncertainty. In the terminology of *Guide to the expression of uncertainty in measurement* (GUM) [1], the uncertainty of the measurement ideally will capture all contributions from both random and systematic effects, that is, all “influence quantities” will be accounted for in the mathematical model that transforms observations into the measurement result. A mathematical model is presented here for isotope ratio analysis by simultaneous ion beam measurements with multi-collector mass spectrometers. This model includes most of the influence quantities that contribute to the uncertainty on the result of such measurements.

Very high precision measurements are possible with multi-collector mass spectrometers because any variations in ion beam intensity are recorded simultaneously on different collectors for each isotope. This technology allows excellent intra-analysis repeatability, which is commonly termed the internal precision. Most analysts, having recognized that the internal precision does not capture the inter-analysis repeatability, will determine the dispersion on repeated analyses of a common sample type, and report this so-called “external precision” as the uncertainty for those measurements. The difficulty that arises in

applying this scheme to mass spectrometry analyses for safeguards is that there is no “common type” of sample. Each sample, especially environmental monitoring samples, is unique. They have widely diverse uranium and plutonium concentrations and isotopic ratios, and the critical measurement parameters that might allow the application of external precision, such as ion beam intensity, cannot be controlled. Therefore, it is necessary to apply the principles of GUM as rigorously as possible.

2. The general equation for measurement of an isotope ratio

The atomic ratio of isotope A to isotope B , $R_{A/B}$ is

$$R_{A/B} = K_{A/B} \frac{1}{n} \sum_{i=1}^n \frac{A_i}{B_i} \quad (1)$$

In Eq.1, $K_{A/B}$ is a correction factor that varies depending on the isotope ratio, and A_i and B_i are the corrected ion beam signals. For multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS), $K_{A/B}$ is the mass bias correction factor, which is empirically determined for a particular instrumental session through the measurement of standard reference materials. For thermal ionization mass spectrometry (TIMS), $K_{A/B}$ is the fractionation factor, which is usually determined by independent measurements of standard reference materials that are analyzed using the same instrumental protocols and under the same physical conditions as the sample measurements. The subscript i on A_i and B_i refers to the individual measurements of the signal. Generally, ion beam intensities are integrated for a time period, for example 5 seconds, and multiple integrations (n of them) are recorded. The simple arithmetic mean of the ratios obtained for each time period is calculated. A measure of the repeatability of these measurements is calculated as the standard uncertainty on the mean and is an important part of the combined standard uncertainty, but it is only one component. A_i and B_i have embedded within them other corrections which must be considered.

$$A_i = G_A(a_i - c - d - e_i) \quad (2)$$

$$B_i = G_B(b_i - f - g - h_i) \quad (3)$$

In these equations, G_A and G_B are detector calibration factors and it is assumed here that they may be applied to all of the variables inside the parentheses. These factors depend on the ratio and the detectors used. They may be simply the Faraday cup relative gain factors (the pre-amplifier gains), or they may be empirically determined detector efficiencies or relative detector efficiencies, or they may be a combination of both. The instrument detector readings, a_i and b_i , are further corrected for detector baseline (let these be c and f), for instrumental background (let these be d and g), and for any signal that may originate from a spike isotope which needs to be subtracted from the sample (let these be e_i and h_i). Alternative calculations of spike subtraction may be formulated, but the contribution to the combined standard uncertainty from spike subtraction is expressed more simply in this way. $K_{A/B}$, G_A , G_B , a_i , b_i , e_i and h_i are all functions themselves of additional parameters, while the detector baselines and blank corrections, c , d , f and g may be calculated more simply. Of course, it is possible to consider additional influence quantities for the detector baselines and blanks and these should be incorporated also, if they are considered to be important. These variables and the method of assigning standard uncertainties to them are given in the following section.

3. The expanded equation and assignment of standard uncertainties

Expanding Eq.1, the mathematical model becomes

$$R_{A/B} = K_{A/B} \frac{G_A}{G_B} \frac{1}{n} \sum_{i=1}^n \frac{(a_i - c - d - e_i)}{(b_i - f - g - h_i)} \quad (4)$$

Note that G_A and G_B have been taken outside the summation, which is allowable given the assumption made in Eq. 2 and Eq. 3, noted above, that they apply to all components within the parentheses. Table 1 describes the variables in more detail and gives a method that can be used to assign their standard uncertainties. For the variables that are themselves functions, the parameters they depend on are noted in this table and the sub-functions are given below.

Table 1. The variables of the general equation for measurement of isotope ratios and methods for determining their standard uncertainties.

Variable	Description	Uncertainty Type and Method used to assign standard uncertainty	Dependent on other parameters?
$K_{A/B}$	For MC-ICPMS, this is the instrumental mass bias correction factor for the ratio A/B . The value is particular to a given measurement session. For TIMS, this is the fractionation factor determined empirically by analysis of standard reference materials.	Usually Type A: Calculated from replicate measurements of certified reference materials. Sometimes Type B: For MC-ICPMS, to prevent underestimation when replications are limited, a pooled estimate from historical data of the variability of the standards may be used in the calculations.	Yes. This factor depends on measurements of CRMs and on the certified values for the standards. A function for MC-ICPMS is given below.
G_A, G_B	The efficiency/gain factors for the detectors used to measure isotope A and B . Ideally, these factors transform counts per second to ions per second, but in reality, it is only important that the magnitude of G_A relative to G_B be accurate.	Usually Type A: Determined from calibration measurements, and may be derived from the same CRM analyses used to define K . As for K , if the range for a limited number of replications is small, then a Type B standard uncertainty based on historical data should be used. (For Faraday detectors, these factors are often automatically included in the raw data and the standard uncertainties are ignored).	Yes, for pulse counting detectors. These factors depend on measurements of CRMs and on the certified values for the standards. A function for MC-ICPMS is given below.
a_i, b_i	The signal intensities for isotope A and B as measured on the detector. For pulse counting detectors, the signal is corrected for dead-time. Common units must be used throughout. Instrument software usually does the conversion and expresses all ion signal intensities in volts, which embeds a constant for the Faraday cup circuit resistance.	Type A: The standard uncertainty may be calculated from counting statistics, but a better method for determining the variability of the signal intensity is to partition the measured uncertainty on the ratio of A/B between the two isotopes. A formula for this partitioning is given in Section 4 below. For pulse counting detectors, the standard uncertainty also includes a component from the dead-time correction.	Yes, for pulse counting detectors dead-time corrections are applied. The function is given below.
c, f	Baseline correction values.	Type B: A sample-specific measurement that is generally made at ± 0.5 amu. The standard uncertainty could be assigned as 20% of the range of these values, for example, to account for the variation in ion tailing from adjacent isotopes.	No. These can be considered as primary variables.
d, g	Instrument background values	Type A: For MC-ICPMS, the value is measured on blank acid solutions immediately prior to and using the same data collection protocols as the sample analysis. For TIMS, these backgrounds may be negligible.	No. These can be considered as primary variables.
e_i, h_i	Spike correction values	Type A: The values are determined by measurements of the spike isotope (C) and knowledge of the A/C ratio in the pure spike. The standard uncertainty is a combination of the uncertainties on these parameters.	Yes. The function is given below.

K The Mass Bias Correction Factor

For MC-ICPMS, an exponential expression is the most commonly used formula for correcting the measured isotope ratio for instrumental mass bias. The correction factor is

$$K_{A/B} = \left(\frac{\text{mass } A}{\text{mass } B} \right)^\beta \quad (5)$$

The exponent, β , is

$$\beta = \frac{\ln\left(\left(\frac{x}{y}\right)_{Std} / \left(\frac{x}{y}\right)_{Meas}\right)}{\ln(\text{mass } x / \text{mass } y)} \quad (6)$$

where the certified or accepted atom ratio of isotope x to isotope y in the standard is $\left(\frac{x}{y}\right)_{Std}$, and the measured ratio of these isotopes in the standard is $\left(\frac{x}{y}\right)_{Meas}$.

Ignoring any uncertainty in the atomic mass of the isotopes, which is very small, the sensitivity coefficients for $K_{A/B}$ are:

$$\frac{\partial K_{A/B}}{\partial \left(\frac{x}{y}\right)_{Std}} = \left(\frac{\text{mass } A}{\text{mass } B} \right)^\beta \frac{\ln(\text{mass } A / \text{mass } B)}{\ln(\text{mass } x / \text{mass } y)} \left[\frac{1}{\left(\frac{x}{y}\right)_{Std}} \right] \quad (7)$$

$$\frac{\partial K_{A/B}}{\partial \left(\frac{x}{y}\right)_{Meas}} = \left(\frac{\text{mass } A}{\text{mass } B} \right)^\beta \frac{\ln(\text{mass } A / \text{mass } B)}{\ln(\text{mass } x / \text{mass } y)} \left[-\frac{1}{\left(\frac{x}{y}\right)_{Meas}} \right] \quad (8)$$

G_A , G_B The Detector Gain Factors

The detector gain or efficiency factors can be determined in several different ways. For a given ratio measurement, they might be a single factor that expresses the relative ion collection and conversion-to-signal efficiencies between two different detectors. For pulse-counting, this might be determined by repeated measurements of a stable ion beam that is magnetically switched between the two detectors.

The method used for most MC-ICPMS analyses at LLNL is to measure two or more ratios simultaneously in a certified reference material. One of these ratios is measured on detectors where the gains are known by other means. For example, the $^{235}\text{U}/^{238}\text{U}$ ratio is measured for CRM U010 on two Faraday cups, where the relative Faraday gain factors are known through electronic calibration of the detection system. This measured ratio can then be used to determine a mass bias correction factor, for $^{234}\text{U}/^{235}\text{U}$ for example, $K_{234/235}$, where ^{234}U is measured on a pulse-counting detector (e.g., *Det1*) and ^{235}U is measured on a Faraday cup.

$$R_{Std.Corr.} = K_{234/235} R_{Std.Meas.} \quad (9)$$

Having $R_{Std.Corr.}$ it is possible to calculate the detector gain factor for *Det1* pulse-counter relative to a Faraday cup. Simplified, this equation is

$$G_{Faraday/Det1} = \frac{R_{Std.Cert.}}{R_{Std.Corr.}} \quad (10)$$

Embedded in this equation are isotope ratio measurements that have almost all of the same functional dependencies as Eq. 4. The standard uncertainty for a single measurement of $R_{Std.Corr.}$ contains these components, and if only one measurement is made, that standard uncertainty should be used. In practice, for MC-ICPMS, multiple analyses of the standard are made during the analytical session, and the average value is used for a given pulse-counting detector. The standard uncertainty on the gain factor is taken as the **larger** of the dispersion of these measurements, or the pooled estimate of the dispersion of the gain factor for that detector based on historical data.

a_i, b_i The Signal Measurements

The correction to a signal for an isotope measured on a pulse-counting detector for the dead-time of that detection system (using a signal for isotope *A*, a_i , as an example) is

$$a_i = \frac{Q_i}{(1 - Q_i \tau)} \quad (11)$$

Where Q_i is the signal from isotope *A* for cycle *i* expressed in counts per second (cps) and τ is the dead-time for that detector in seconds. The sensitivity coefficients for a_i with respect to Q_i and τ are:

$$\frac{\partial a_i}{\partial Q_i} = \frac{1}{(1 - Q_i \tau)^2} \quad (12)$$

$$\frac{\partial a_i}{\partial \tau} = \frac{Q_i^2}{(1 - Q_i \tau)^2} \quad (13)$$

The standard uncertainty for Q_i is calculated from the partitioning equation given below, and the standard uncertainty for the dead-time, τ , is determined when the value is determined. A discussion of methods to determine dead-time is beyond the scope of this document.

e_i, h_i The Spike Corrections

The function for the spike-correction, using e_i for this example, depends on the intensity of the spike isotope, call this C_i , and the ratio of isotope *A* to *C* in the pure spike. In practice, the correction should be made using **biased** values for this ratio, because the calculated correction will be subtracted from the measured signal intensity **before** it is corrected for instrumental mass bias. This formulation assumes that the spike isotope is not present in the un-spiked sample.

$$e_i = \left(\frac{A}{C}\right)_{Biased} C_i \quad (14)$$

The sensitivity coefficients for this equation are $\frac{\partial e_i}{\partial C_i} = \left(\frac{A}{C}\right)_{Biased}$ and $\frac{\partial e_i}{\partial \left(\frac{A}{C}\right)_{Biased}} = C_i$.

Further, $\left(\frac{A}{C}\right)_{Biased}$ is $\left(\frac{A}{C}\right)_{Spike}$ **divided** by $K_{A/C}$, and the standard uncertainty on this ratio will contain a small contribution from the uncertainty on this mass bias correction factor.

4. The partitioning equation

The partitioning equation is used to partition the Type A standard uncertainty measured on the average isotope ratio $\left(\frac{1}{n}\sum_{i=1}^n \frac{A_i}{B_i}\right)$ into components due to A_i and B_i . These components are assigned as the standard uncertainties on a_i and b_i (Eq.4), and are used in the calculation of the combined standard uncertainty. This method of partitioning allows the calculated uncertainty on the ratio to be assigned to the components based on their ion beam intensities, with assurance that, when recombined, they will recapture that Type A calculation. More components are considered using this formulation and the uncertainty budget is more complete. The details follow:

To partition the standard uncertainty, $U_{A/B}$, determined for the isotope ratio A/B measured by simultaneous multi-collection, into uncertainties from the numerator U_A , and from the denominator U_B , use Eq. 15 and 16

$$\left(\frac{U_A}{A}\right)^2 + \left(\frac{U_B}{B}\right)^2 = \left(\frac{U_{A/B}}{(A/B)}\right)^2 \quad (15)$$

$$\frac{U_A}{U_B} = \frac{\sqrt{A}}{\sqrt{B}} \quad (16)$$

Equation 15 is an expression derived from the law of propagation of uncertainty, and Eq. 16 assumes that the uncertainty on the measured ion beam signal is the square-root of that signal, *i.e.*, that it follows a Poisson distribution. Solving for the only two unknowns, U_A and U_B , the solutions to are given by Eq. 17 and 18.

$$U_A = \left(\frac{U_{A/B}}{(A/B)}\right) \sqrt{\frac{B^2 A}{B+A}} \frac{\sqrt{A}}{\sqrt{B}} \quad (17)$$

$$U_B = \left(\frac{U_{A/B}}{(A/B)}\right) \sqrt{\frac{B^2 A}{B+A}} \quad (18)$$

In practice, the units expressing the signal intensity do not matter. The signal intensity can be expressed as counts, a count rate, a voltage or amperage as long as the same units are used for both the numerator and the denominator.

5. The sensitivity coefficients

In the following formulas the summation signs are preserved, because a summation of partial derivatives is equivalent to the partial derivative of the sum. The partial derivatives of Eq. 4 with respect to each variable follow. The summations are all over the total number of measurement cycles, $i = 1$ to n .

First, for the numerator:

$$\frac{\partial R_{A/B}}{\partial K_{A/B}} = \frac{G_A}{G_B} \frac{1}{n} \sum \frac{(a_i - c - d - e_i)}{(b_i - f - g - h_i)} \quad (19)$$

$$\frac{\partial R_{A/B}}{\partial G_A} = \frac{K_{A/B}}{G_B} \frac{1}{n} \sum \frac{(a_i - c - d - e_i)}{(b_i - f - g - h_i)} \quad (20)$$

$$\frac{\partial R_{A/B}}{\partial a_i^*} = K_{A/B} \frac{G_A}{G_B} \frac{1}{n} \sum \frac{1}{(b_i - f - g - h_i)} \quad (21)$$

$$\frac{\partial R_{A/B}}{\partial c} = K_{A/B} \frac{G_A}{G_B} \frac{1}{n} \sum \frac{-1}{(b_i - f - g - h_i)} \quad (22)$$

$$\frac{\partial R_{A/B}}{\partial d} = K_{A/B} \frac{G_A}{G_B} \frac{1}{n} \sum \frac{-1}{(b_i - f - g - h_i)} \quad (23)$$

$$\frac{\partial R_{A/B}}{\partial e_i^*} = K_{A/B} \frac{G_A}{G_B} \frac{1}{n} \sum \frac{-1}{(b_i - f - g - h_i)} \quad (24)$$

And then the denominator:

$$\frac{\partial R_{A/B}}{\partial G_B} = K_{A/B} G_A \frac{1}{n} \sum \frac{-(a_i - c - d - e_i)(b_i - f - g - h_i)}{[G_B(b_i - f - g - h_i)]^2} \quad (25)$$

$$\frac{\partial R_{A/B}}{\partial b_i} = K_{A/B} \frac{G_A}{G_B} \frac{1}{n} \sum \frac{-(a_i - c - d - e_i)}{(b_i - f - g - h_i)^2} \quad (26)$$

$$\frac{\partial R_{A/B}}{\partial f} = K_{A/B} \frac{G_A}{G_B} \frac{1}{n} \sum \frac{(a_i - c - d - e_i)}{(b_i - f - g - h_i)^2} \quad (27)$$

$$\frac{\partial R_{A/B}}{\partial g} = K_{A/B} \frac{G_A}{G_B} \frac{1}{n} \sum \frac{(a_i - c - d - e_i)}{(b_i - f - g - h_i)^2} \quad (28)$$

$$\frac{\partial R_{A/B}}{\partial h_i} = K_{A/B} \frac{G_A}{G_B} \frac{1}{n} \sum \frac{(a_i - c - d - e_i)}{(b_i - f - g - h_i)^2} \quad (29)$$

It is relatively simple to make these calculations on a cycle-by-cycle basis, and it is the accurate way to determine the values of these sensitivity coefficients. They could be calculated using an average value for each variable, which simplifies to a set of 11 calculations (instead of $11 \times n$), but the calculation of the uncertainty will be only approximate. This is because the mean of ratios **does not equal** the sum of the numerators over the sum of the denominators.

$$\frac{1}{n} \sum_{i=1}^n \left(\frac{x_i}{y_i} \right) \neq \frac{\sum_{i=1}^n x_i}{\sum_{i=1}^n y_i} \quad (30)$$

Once the values of the sensitivity coefficients and the standard uncertainties of the input parameters are determined, the combined standard uncertainty on $R_{A/B}$ is simply calculated according to GUM.

6. Conclusions

It is important that the uncertainties on isotope ratio measurements used for IAEA safeguards be a complete and accurate representation of the quality and reliability of the results, so that any conclusions

that are drawn or actions that may be taken based on these measurements rest on a firm metrological foundation. Because all environmental samples taken for safeguards are unique, the calculation of the uncertainty for mass spectrometric measurements of these samples must rely on first principles, and a rigorous application of GUM. The equations given in this paper are the applications of these principles that have been developed and adopted at LLNL for analyses of bulk environmental samples collected for IAEA safeguards.

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